Cross-linked polyelectrolyte for direct methanol fuel cells applications based on a novel sulfonated cross-linker

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HIGHLIGHTS

- Cross-linker with proton conductive group was designed and synthesized.
- A comparison between the sulfonated and non-sulfonated cross-linkers was made.
- By using the sulfonated cross-linker, SPEEK has been successfully modified.
- The result membranes showed low methanol crossover as well as high conductivity.
- The oxidative stability of the result membranes was much improved also.

ARTICLE INFO

ABSTRACT

A novel type of cross-linked proton exchange membrane of lower methanol permeation and high proton conductivity is prepared, based on a newly synthesized sulfonated cross-linker: carboxyl terminated benzimidazole trimer bearing sulfonic acid groups (s-BI). Compared to membranes cross-linked with non-sulfonated cross-linker (BI), SPEEK/s-BI-n membranes show higher IEC values and proton conductivities. Meanwhile, oxidative stability and mechanical property of SPEEK/s-BI-n membranes are obviously improved. Among SPEEK/s-BI-n membranes, SPEEK/s-BI-2 exhibits high proton conductivity, low swelling ratio (0.122 S cm^{-1} and 15.2% at 60 °C, respectively) and low methanol permeability coefficient. These results imply that the cross-linked membranes prepared with the newly sulfonated cross-linker are promising for the direct methanol fuel cells (DMFCs) application.

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1. Introduction

Direct methanol fuel cells (DMFCs) have gained great attention as a candidate for future portable power devices for their advantages, such as high energy density and simple system [1–3]. However, there are still several challenging technical problems hindering its commercialization. One major obstacle is excess methanol permeates through the polyelectrolyte, which severely harms its cell performance [2,4]. Nafion 117 has been considered as the most promising electrolyte material for DMFC [5]. However, it still shows drawbacks of high methanol permeability, unacceptable manufacturing cost and complicated production process. Sulfonated aromatic polymers have been studied as alternatives to Nafion [6–10]. Among them, sulfonated poly(ether ether ketone) is

considered to be one of the most promising candidates because of its low cost and facile preparation process [11–13]. In the case of sulfonated poly(ether ether ketone), adequate acidic groups are required to obtain sufficient proton conductivity. However, high sulfonation degree always leads to an increase in methanol crossover as well as a decline of the dimensional stability [14–16].

Cross-linking has been proved to be an easy and effective method to suppress excess methanol permeation and enhance the dimensional stability of membranes [17–21]. However, cross-linked membranes usually show decreased conductivity compared to the corresponding pristine ones, owning to two factors: 1) the relatively compact molecular structures always restrain the mobility of protons as well as lower water content in membranes [22]; 2) Nonconductive cross-linker dilutes the density of sulfonic acid groups, leading to lower proton conductivity. Yen et al. investigated the properties of membranes containing polyhedral oligomeric silsesquioxane cross-linkers with or without sulfonic acid groups, and found that membranes contained the cross-linker

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with sulfonic acid groups showed better separation of hydrophilic domains [23].

In our previous work, we used carboxyl-terminated benzimidazole trimer as a cross-linker to prepare cross-linked membranes which showed enhanced stability but slightly lowered conductivity [24]. In this work, a sulfonated cross-linker, carboxyl-terminated benzimidazole trimer bearing sulfonic acid groups (s-BI), was designed and synthesized. The cross-linkers with proton conductive groups could maintain the ion exchange capacities of the membranes and act as supplements of the proton carriers on the main chain. The properties of the cross-linked membranes related to fuel cell applications were investigated in detail and the feasibility of this method was confirmed.

2. Experimental

2.1. Materials

3, 3′-diaminobenzidine (DAB) was purchased from Shanghai Kexing Biological Technology Co., Ltd., China. 5-sulfoisophthalic acid sodium salt (s-IPA, 95%) was obtained from Sigma–Aldrich Ltd. Isophthalic acid (IPA) was supplied by Aladdin Reagents (Shanghai) Co., Ltd. SPEEK (DS = 0.73) was prepared via post-sulfonation of PEEK according to the procedure described in literature [25]. Poly(phosphoric acid) (PPA), Dimethyl sulfoxide (DMSO) and other reagents were obtained commercially and used without further purification.

2.2. Synthesis of s-BI

The synthesis of s-BI in lithium form (s-BI–Li) was following the typical coupling reaction (Scheme 1): 1.3928 g DAB (6.5 mmol), 4.1934 g s-IPA (15.6 mmol) and 106 g PPA were added to a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a reflux condenser. The mixture was heated to 140 °C and kept for 3 h to form homogeneous solution. Then, it was slowly heated to 190 °C and maintained at this temperature for 15–20 h. The dark brown solution was poured into a

large excess of deionized water. The brown powder obtained was then washed thoroughly with deionized water and neutralized with lithium hydroxide to obtain s-BI–Li.

Carboxyl-terminated benzimidazole trimer (BI) was synthesized in similar procedure.

2.3. Preparation of the cross-linked membranes (SPEEK/s-BI-n)

The SPEEK/s-BI-n membranes were prepared via solution casting method and followed thermal treatment. Take SPEEK/s-BI-1 for example, 0.98 g SPEEK and 0.02 g s-BI–Li were first dissolved in 10 mL DMSO. The solution was cast onto a glass plate and dried at 60 °C for 24 h. The hydrogen form membranes were obtained after immersing the obtained membrane in 1 M HCl for 24 h and washed with deionized water thoroughly. The cross-linking reaction was performed by heating the membranes at 160 °C for 12 h in vacuum oven. Fig. 1 illustrated the component and cross-linking method of the membranes.

Cross-linked SPEEK membranes with BI (SPEEK/BI-n) were also prepared using the above method. BI molar ratio in SPEEK/BI-n was equal to the molar ratio of s-BI in the corresponding SPEEK/s-BI-n membrane. The component of each membrane is showed in Table 1.

2.4. Characterization and measurements

2.4.1. Structural characterization
^{1}H NMR spectra were measured on an AVANCE 500 at room temperature, using DMSO-d_6 as solvent and tetramethylsilane (TMS) as the standard. FT-IR spectra were recorded on a Nicolet Impact 410 Fourier transform infrared spectrometer using KBr disc.

2.4.2. Thermal property
The thermal property of the cross-linked membranes was investigated by a Perkin–Elmer TGA. 3–5 mg samples were heated at 120 °C for 15 min to remove residue solvent and water. They were then cooled to 80 °C and reheated to 700 °C at a heating rate of 10 °C min^{-1} under N$_2$.

#### 2.4.3. Ion exchange capacities (IECs)
The IECs of the cross-linked membranes was obtained by the titration method. The membranes in acid-form were dried at 120 °C under vacuum for 24 h, weighed, and immersed in 1 M NaCl solution at room temperature for 24 h to undergo an ion-exchange process. The H$^+$ ions in the solution were then titrated with a standardized NaOH solution using phenolphthalein as an indicator. The ion-exchange capacity was calculated from the formula as follows:

$$IEC = \frac{\text{volume of consumed NaOH} \times \text{molarity of NaOH}}{\text{weight of dried membrane}} \tag{1}$$
$$\left(\text{mequiv} \bullet \text{g}^{-1}\right)$$

2.4.4. Water uptake, methanol solution uptake and swelling ratio
Water uptake and swelling ratio were determined from the weight and thickness differences between the dry and wet membranes. In details, the membranes were dried at 120 °C for several hours until constant weights and lengths were obtained. And then the dried membranes were placed in water vessels at desired temperature for 24 h. The wet membranes were wiped with tissue paper and quickly weighed and measured. The water uptake and swelling ratio of the membranes were calculated from the following equations:
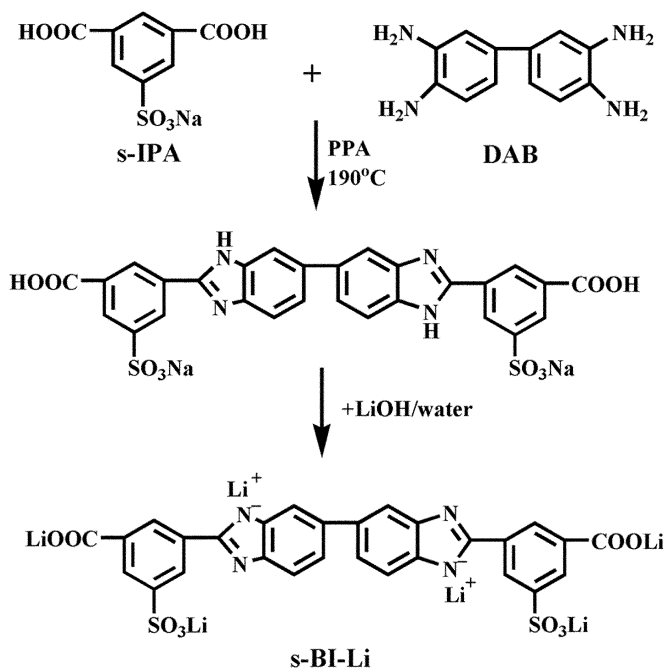
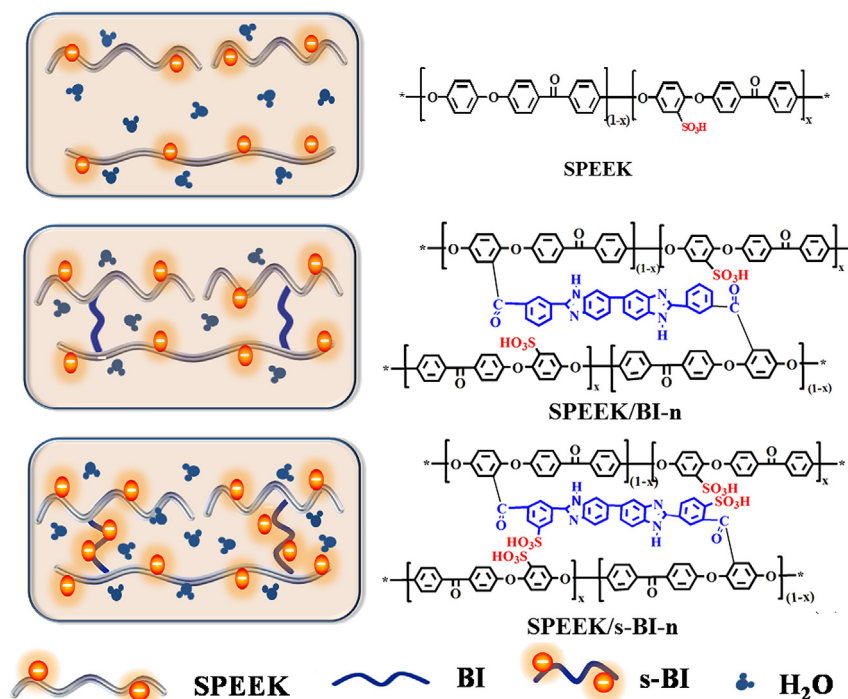**Scheme 1.** Synthesis of cross-linker with sulfonic acid groups (s-BI).

Fig. 1. The structure schematic of SPEEK, SPEEK/BI-n and SPEEK/s-BI-n membranes.

$$\text{Water uptake}(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (2)$$

$$\text{Swelling ratio}(\%) = \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100 \qquad (3)$$

where W_{dry} and W_{wet} are the weights of the dry and wet membranes, respectively. T_{dry} and T_{wet} are the thicknesses of the dry and wet membranes, respectively.

The similar test was carried out in 10 mol L^{-1} methanol aqueous solution. The samples were immersed into the above solution at room temperature for 24 h. Membranes' weight and thickness changes were recorded. The methanol solution uptake and swelling ratio were calculated in the similar method with the water uptake and swelling ratio, respectively.

2.4.5. Proton conductivity and methanol permeability

The membrane proton conductivity was measured using a four-electrode alternating current impedance method. Samples were immersed in deionized water for 24 h before test to remove the ion might contain. The measurement was carried out in 100% humidity. Impedance values were determined using Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ) over a frequency range of 0.1–100 kHz.

Proton conductivity was calculated with following equation:

$$\sigma = \frac{L}{R \times A} \qquad (4)$$

where σ (S cm^{-1}) is the proton conductivity, R is resistance of the membrane. A is the cross-sectional area of the membrane. And L is the distance between the two electrodes.

The methanol permeability coefficient D_K (cm^2 s^{-1}) was measured by using a two-chamber diffusion cell described in our previous study [26]. The chambers separated by the measured membrane were filled with 10 M methanol solution (150 mL) and deionized water (150 mL) respectively. To ensure uniformity, magnetic stirrers were applied in each compartment. The concentration of methanol in the water chamber was measured using SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_B(t) = \frac{A}{V_B}\frac{D_K}{L}C_A(t - t_0) \qquad (5)$$

2.4.6. Oxidative stability

The oxidative stability was evaluated by the following method: the dry samples were immersed in 3% hydrogen peroxide, 2 ppm $FeSO_4$ solution at 60 °C and recorded the time that the samples started to be broken and the weight loss after 1 h.

2.4.7. Mechanical property

The mechanical properties of the membranes were determined from stress–strain curves measured by SHIMADZUAG-I 1KN at a strain rate of 2 mm min^{-1}. The size of film specimens was 15 mm × 4 mm. For each testing, at least four samples were used and the average values were calculated.

3. Results and discussion

3.1. Synthesis of s-BI

As shown in Scheme 1, s-BI was synthesized through a typical coupling reaction in PPA. To avoid the multi molecular weight dispersion, excess s-IPA was used and mixed adequately with DAB before elevating the temperature. In order to enhance the solubility of s-BI in organic solvent, lithium hydroxide was used to transform s-BI into s-BI–Li. s-BI–Li can be easily dissolved in water and dimethylsulfoxide (DMSO). The structure of s-BI–Li was confirmed

Table 1
Component, IEC, proton conductivity, methanol permeability and selectivity of membranes.

Membrane	Cross-linker content (wt%)	λ^a	IEC (mequiv g^{-1})	Swelling ratio[b] (%)	Water uptake[b] (%)	Proton conductivity[b] (S cm^{-1})	Methanol permeability (cm^2 s^{-1})	Selectivity (Ss cm^{-3})
SPEEK/s-BI-1	2.00	0.01	1.92	52.7	86.0	0.150	9.03×10^{-8}	5.75×10^{5}
SPEEK/BI-1	1.42	0.01	1.79	22.4	81.3	0.122	8.67×10^{-8}	5.65×10^{5}
SPEEK/s-BI-2	10.00	0.06	1.81	15.2	82.1	0.122	7.95×10^{-8}	5.53×10^{5}
SPEEK/BI-2	7.29	0.06	1.36	16.6	42.6	0.037	4.83×10^{-8}	3.72×10^{5}
SPEEK/s-BI-3	20.00	0.14	1.57	11.4	63.2	0.062	8.50×10^{-8}	2.29×10^{5}
SPEEK/BI-3	15.04	0.14	0.94	2.0	28.7	0.027	1.22×10^{-8}	1.26×10^{6}
SPEEK	0	0	1.80	—[c]	—[c]	0.170	11.3×10^{-8}	4.69×10^{5}

[a] The molar ratio of cross-linker/SPEEK unit in membranes.
[b] Tested at 60 °C in deionized water.
[c] Membrane was over swelling and could not be measured.

by ^{1}H NMR spectrum. As shown in Fig. 2, each hydrogen atom in the structure was identified well, which sufficiently attested to the successful synthesis of s-BI–Li.

3.2. Membrane preparation and characterization

The cross-linked network in the membrane was constructed via Friedel–Crafts reaction as illustrated in Fig. 1. The mechanism of the cross-linking reaction was depicted in our previous work [27]. We employed FT-IR to verify the formation of the cross-linked structure. As shown in Fig. 3a, after adding s-BI into the polymers, typical absorption bands around 1716 cm^{-1} could be observed which were corresponding to carboxylic acid groups [27]. It was because the cross-linking reaction could not complete thoroughly and there were some residuals of carboxylic acid groups. Fig. 3b shows the FT-IR spectra of heated and unheated SPEEK/s-BI-2, respectively. Since PEEK backbone contains a lot of keto groups, the generated keto groups after cross-linking could not be reflected obviously by FT-IR. However, after heating the peak around 1716 cm^{-1} turned to smooth, which indicated a great amount of carboxylic acid groups in s-BI had been consumed during the cross-linking process.

Although both SPEEK and s-BI–Li can be easily dissolved in water, membranes after cross-linked could not, which further proved the construction of cross-linked network in the membranes.

3.3. Thermal stability and mechanical properties

The thermal stabilities of SPEEK and cross-linked membranes with different cross-linking degree were investigated by TGA. As seen in Fig. 4, all of the membranes displayed excellent thermal stabilities. Two degradation steps can be observed from all the curves. The first one, approximately from 305 °C to 400 °C, was attributed to the decomposition of sulfonic acid groups. The second one, started at about 450 °C, was caused by the decomposition of the polymer main chain. It was obvious that the cross-linked membranes showed higher decomposition temperature than

pristine SPEEK. With the increasing of cross-linker content, 5% weight loss temperature increased from 337 °C to 356 °C. This phenomenon might be attributed to the restriction of sulfonic acid groups by benzimidazole moieties through the acid–base interaction. Meanwhile, the mobility of the polymer molecular was
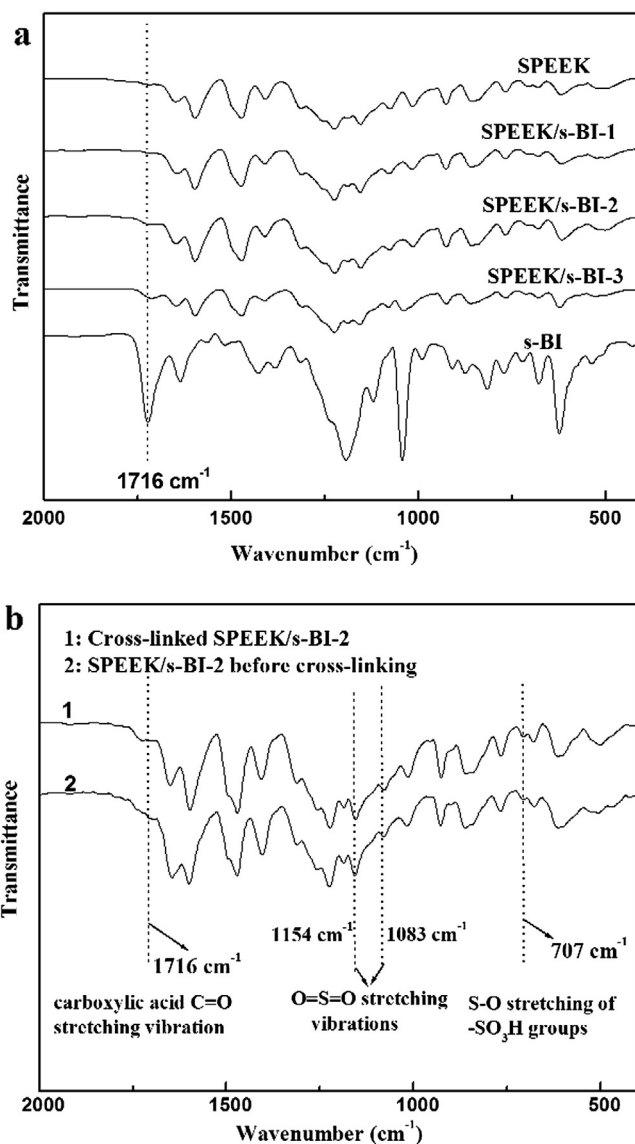

Fig. 2. ^{1}H NMR spectrum of s-BI-Li.

Fig. 3. FT-IR spectra of a: s-BI, SPEEK and cross-linked membranes SPEEK/s-BI-1, 2, 3; b: SPEEK/s-BI-2 membrane before cross-linking and after cross-linking treatment.
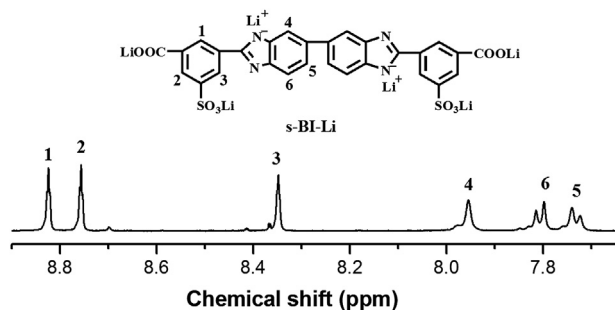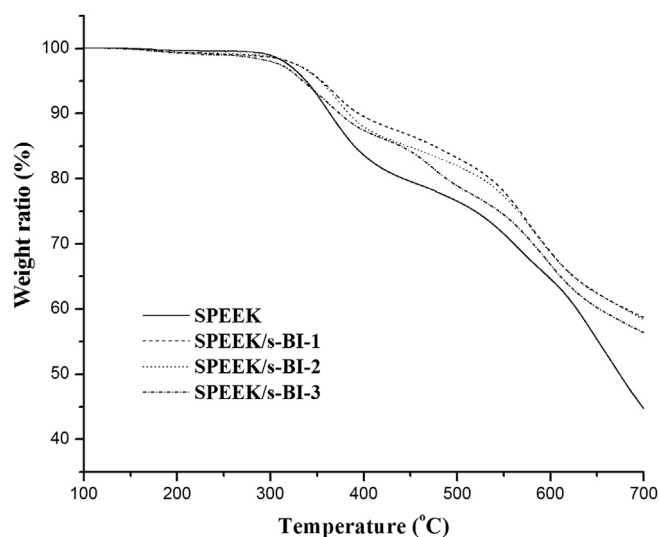
Fig. 4. TGA curves of SPEEK and SPEEK/s-BI-n.

restricted by the cross-linked network and the main chain decomposition temperature increased as well. TGA results demonstrated that the combination of cross-linked network and s-BI group improved the thermal stability of the membranes.

Table 2 lists the mechanical properties of pristine SPEEK, SPEEK/BI-n and SPEEK/s-BI-n. The Young's modulus and tensile strength of the SPEEK/s-BI-n membranes were in ranges of 2.2—3.5 GPa and 66—69 MPa, respectively. They increased with the raise of cross-linkers content and were higher than that of pristine SPEEK membrane. This result further reflected the acid—base interaction in the membranes and the restriction of polymer mobility by the cross-linked network. The membranes of SPEEK/BI-n had slightly better mechanical properties than SPEEK/s-BI-n membranes. This result should be attributed to the higher sulfonic acid group content in the latter type. However, the mechanical properties of the SPEEK/s-BI-n membranes were greatly superior to the pristine SPEEK membrane. This result means the cross-linked network enhanced membrane resistance to fracture and deformation, which agrees well with results in literature [28].

3.4. Oxidative stability

The oxidative stability has a strong effect on the lifetime of PEMFC [29]. The degradation of the polymer is assumed to be caused by the attack from radicals. Fenton's reagent was usually used to mimic the environment in operating fuel cells, which was more rigorous than the real operating condition [30]. An accelerated test used hot Fenton's reagent was employed to evaluate the oxidative stability of SPEEK and SPEEK/s-BI-n membranes. The results were shown in Table 3. SPEEK/s-BI-n showed much better oxidative durability compared to the pristine membrane. The

SPEEK membrane began to break in less than 30 min and dissolved within 45 min. However, all the SPEEK/s-BI-n membranes kept intact and remained more weight than the pristine polymer after 1 h. The improved oxidative stability of SPEEK/s-BI-n might be attributed to: 1) Cross-linking structure made the membranes more compact, which possess better resistance to the degradation. 2) Benzimidazole groups can trap the free radicals and retard the degradation process [31].

3.5. Ion-exchange capacity (IEC), dimensional stability and conductivity

Ion-exchange capacity (IEC) directly reflects ion conductor concentration in membranes. It is a key parameter for evaluating membrane performance [32]. IEC values of the cross-linked membranes varied with the molar ratio of the cross-linker to SPEEK unit were depicted in Fig. 5. The IEC values of SPEEK/BI-n membranes showed a decline from 1.79 to 0.94 mequiv g^{-1} with the increasing of BI content. The decline might be attributed to two factors: 1) the acid—base interaction between benzimidazole and $-SO_3H$ decreased the amount of free sulfonic acid groups available to release protons. 2) benzimidazole-based cross-linker diluted the density of $-SO_3H$ that led to the lower IEC indirectly. As expected, the IEC values of SPEEK/s-BI-n were much higher than those of SPEEK/BI-n and did not show any decrease compared to the pristine membrane when $\lambda < 0.06$. It illustrated that the cross-linker with sulfonic acid groups could compensate the acid consumption in the acid—base interactions at certain extent.

Cross-linking is an effective approach to improve the dimensional stability. As expected, all the cross-linked membranes exhibited better dimensional stabilities compared to SPEEK membrane, and larger amount of cross-linker resulted in lower water uptake and lower swelling ratio. Fig. 6 shows the water uptakes and swelling ratios of membranes with similar IEC values (SPEEK/s-BI-2 and SPEEK/BI-1) at different temperatures. Both of the water uptake and the swelling ratio rose with temperature. It was obvious that the water uptake of SPEEK/s-BI-2 was higher than SPEEK/BI-1, indicating that the cross-linkers with sulfonic acid groups enhanced the water sorption. Despite absorbing more water, SPEEK/s-BI-2 exhibited lower swelling ratio compared to SPEEK/BI-1, which could be attributed to the fact that higher doping amount of the cross-linker resulted in greater restriction in the matrix. This result indicated that the introduction of cross-linkers with sulfonic acid groups could enhance dimension stability as well as water sorption ability, which ensured moderate water for proton conducting process. This phenomenon was one of our main purposes for using the cross-linkers bearing sulfonic acid groups.

As reported in previous works, in addition to the indirect effect of cross-linking on conductivity through water uptake, conductivity could also be lowered immediately by the compact structures of cross-linked membranes [33]. However, this effect could be largely offset by using the cross-linker s-BI according to our results. This could be substantiated by Fig. 7, where SPEEK/s-BI-2 and SP2EEK/BI-1 showed similar conductivities in the whole test temperature

Table 2
Mechanical properties of SPEEK, SPEEK/s-BI-n and SPEEK/BI-n membranes.

Membranes	Tensile strength (MPa)	Young's modulus (GPa)	Maximum elongation (%)
SPEEK	55.78	2.13	16.03
SPEEK/s-BI-1	66.50	2.23	28.24
SPEEK/s-BI-2	66.23	2.62	13.40
SPEEK/s-BI-3	69.22	3.20	3.70
SPEEK/BI-1	70.34	2.49	14.15
SPEEK/BI-2	76.08	2.37	12.70
SPEEK/BI-3	89.35	3.50	18.57

Table 3
Oxidative stabilities of SPEEK/s-BI-n and SPEEK membranes.

Membranes	Oxidative time[a] (min)	Remaining weight[b] (%)
SPEEK	25	0
SPEEK/s-BI-1	89	14.1
SPEEK/s-BI-2	112	32.2
SPEEK/s-BI-3	239	89.0

[a] The expended time of breaking into pieces.
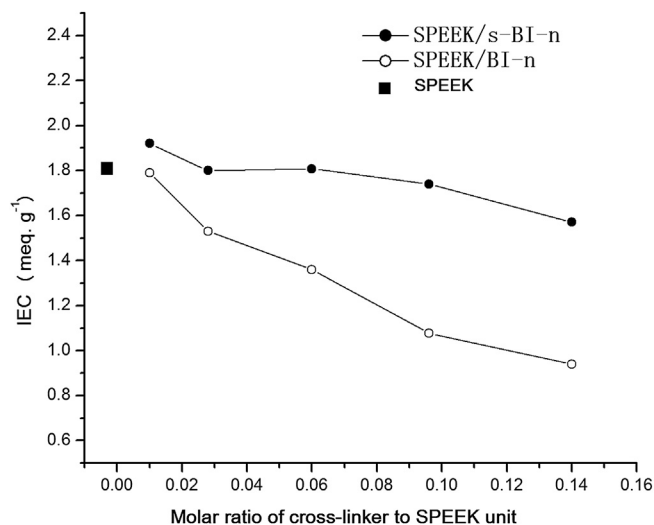[b] The remaining weight of the membranes after treated for 1 h.

Fig. 5. The IEC values of SPEEK/s-BI-n and SPEEK/BI-n varying with the content of the cross-linkers.

Fig. 7. Proton conductivity of all the membranes at different temperatures.

range, although the cross-linker content of SPEEK/s-BI-2 was much higher than that of SPEEK/BI-1. This phenomenon could be explained by the good water-sorption ability of SPEEK/s-BI-2. SPEEK/s-BI-n always showed higher conductivity than that of SPEEK/BI-n when the λ values were the same. Among these membranes, SPEEK/s-BI-2 showed much higher conductivities compared to Nafion at the test temperatures [34]. At 60 °C, the membrane had a conductivity of 0.122 S cm^{-1}, maintained an ideal dimensional stability. All these results verified the effectiveness of s-BI cross-linker on the modification of SPEEK membranes. However, the conductivity of SPEEK/s-BI-3 was severely affected by the cross-linked structure. This result indicated that 10% could be an appropriate content of s-BI cross-linker. The proton conductivity activation energy (Ea) of SPEEK/s-BI-n was calculated through Arrhenius Equation and showed in Fig. 8. The Ea of cross-linked membranes was lower than that of pristine SPEEK membrane and displayed a decline with the increasing of cross-linker content. This result further testified that the introduction of cross-linker with sulfonic acid groups could make proton transfer easier.
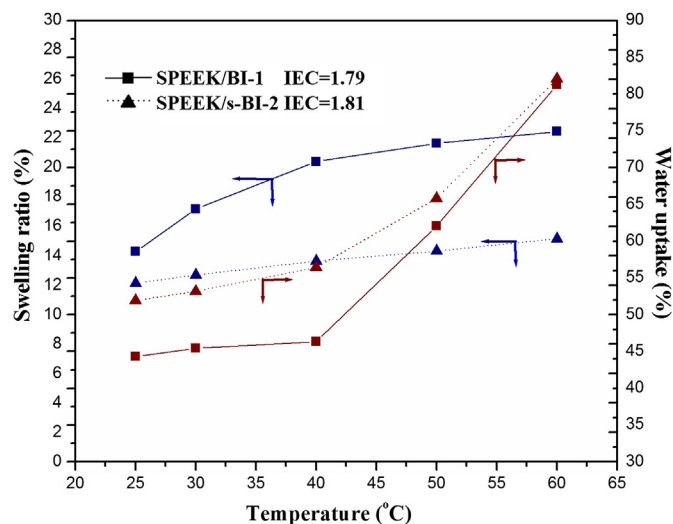
3.6. Methanol solution uptakes, swelling ratios and mechanical properties

The methanol solution uptakes and swelling ratios of SPEEK and SPEEK/s-BI-n membranes in methanol solution with high concentration (10 mol L^{-1}) were measured, as well as the mechanical properties of the membranes after immersing in methanol solution. It should be noticed that the concentration of the methanol solution is quite higher than that in actually operating condition. The swelling ratios, solution uptakes and the mechanical properties were listed in Table 4. Unlike the cross-linked membranes, pristine SPEEK membrane was over swelling and cannot be picked up. From the data, we can see the swelling ratio of cross-linked membranes decreased (from 78.0% to 74.1%) with the increasing of s-BI content. The same trend was showed in solution uptakes of the membranes. The mechanical properties of the swelling membranes were tested in wet status. It was not strange that the mechanical properties of the cross-linked membranes were reduced compared to dry membranes, but still much better than the pristine SPEEK membrane, which was not measurable. Overall, these results demonstrated that the cross-linked network in the membranes enhanced dimensional and mechanical stabilities of the membranes not only in pure water but also in the methanol aqueous solution.
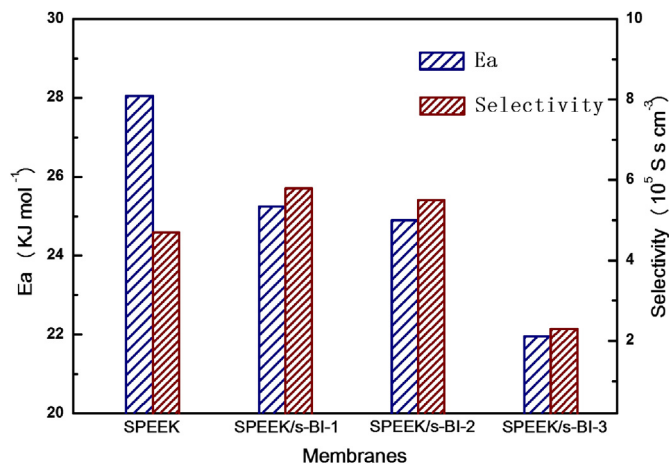

Fig. 6. Swelling ratio and water uptake of SPEEK/s-BI-2 and SPEEK/BI-1.

Fig. 8. The activation energy and selectivity of SPEEK and SPEEK/s-BI-n membranes.

Table 4
Solution uptake, swelling ratio and mechanical properties of SPEEK/s-BI-n membranes after immersing in methanol water solution (10 mol L^{-1}).

Membranes	Swelling ratio (%)	Solution uptake (%)	Tensile strength (MPa)	Young's modulus (MPa)	Maximum elongation (%)
SPEEK/s-BI-1	78.0	374.6	2.6	8.46	100.905
SPEEK/s-BI-2	76.1	334.9	3.8	9.24	107.709
SPEEK/s-BI-3	74.1	326.8	2.9	9.62	94.58

3.7. Methanol resistance and selectivity

Polymer electrolyte membranes for DMFC must possess both high proton conductivity and effective methanol resistance [35]. As shown in Table 1, all the SPEEK/s-BI-n membranes showed similar methanol permeability coefficient (about 8×10^{-8} to 9×10^{-8} cm^2 s^{-1}), and all the results were superior to pristine SPEEK membrane. Cross-linkers in the system tightened the structure of the composite membranes, leading to a more compact membrane structure that effectively resisted methanol penetration. Besides, since the sulfonic acid groups in s-BI were involved in the formation of the hydrophilic domains and the methanol permeation took place through the hydrophilic cluster channels [36], SPEEK/s-BI-n showed higher methanol permeability than SPEEK/BI-n. Among all the membranes, SPEEK/s-BI-2 with good performance in conductivity and dimensional stability displayed a methanol permeability coefficient of 7.95×10^{-8} cm^2 s^{-1}, which was only one twelfth of the value of Nafion (10.05×10^{-7} cm^2 s^{-1}) [37].

Selectivity (the ratio of proton conductivity to methanol permeability coefficient) is an important parameter for appraising the potential performance of DMFC membranes [38]. SPEEK/s-BI-2 had an outstanding selectivity of 5.5×10^5 S s cm^{-3}, which was much higher than that of Nafion (7.06×10^4 S s cm^{-3}). This result indicated that the cross-linked membrane possessed excellent comprehensive properties had the potential to be used in DMFCs.

4. Conclusions

A series of cross-linked membranes (SPEEK/s-BI-n) have been prepared via a simple and feasible method, based on a newly synthesized sulfonated cross-linker. The cross-linked SPEEK/s-BI-n membranes showed outstanding stability and lower swelling ratio compared to the pristine SPEEK membranes. Meanwhile, sulfonic acid groups in the cross-linker endowed the SPEEK/s-BI-n membranes with comparable IEC values to the pristine SPEEK membrane, as well as sufficient conductivity. Especially, SPEEK/s-BI-2 displayed a high proton conductivity of 0.122 S cm^{-1} at 60 °C and a low methanol permeability coefficient which was only one twelfth of Nafion. Furthermore, SPEEK/s-BI-2 exhibited outstanding stability and lower swelling ratio. All the results indicate that the cross-linked membranes prepared in this facile way are promising candidates for DMFCs application.

Acknowledgments

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